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Regioselective Synthesis of Biradical Negative Ions in the Gas Phase. Generation of Trimethylenemethane, *m*-Benzyne, and *p*-Benzyne Anions

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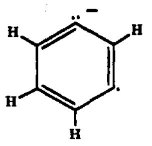
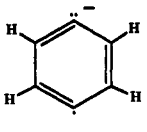
We wish to report a general, regioselective method for producing high yields of biradical negative ions ("distonic" radical anions) in the gas phase. These species are of fundamental interest for several reasons: for use in mass spectrometric studies of free radical chemistry,[1] for use in investigating the acid–base properties of radicals,[2,3] and, most significantly, for use in negative ion photoelectron spectroscopic measurements of the electron affinities and singlet–triplet energy gaps in the corresponding neutral biradicals.[4,5] We describe here the mechanism and scope of the new synthetic procedure and its application in the synthesis and characterization of *m*- and *p*-benzyne anions (**1** and **2**) and trimethylenemethane anion (**3**) in a flowing afterglow–triple quadrupole apparatus.[6]



1



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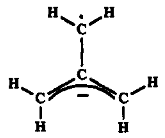
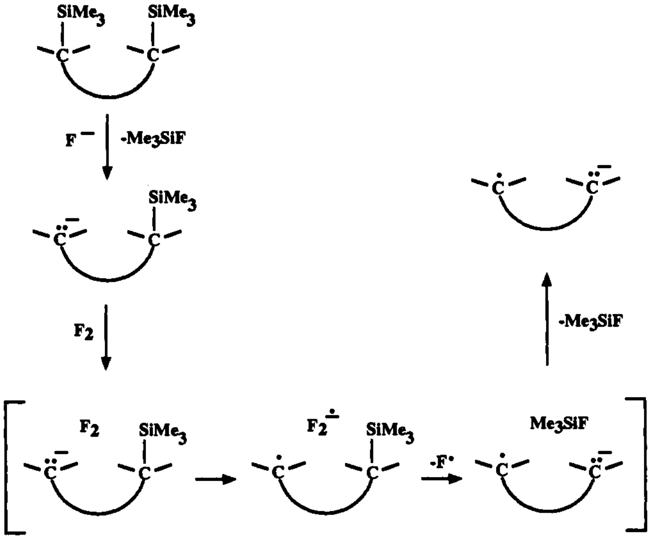


3

A common method of forming biradical and carbene negative ions in the gas phase is 1,*n* (*n* = 1, 2, 3, ...) abstraction of $H_2^{\bullet+}$ from hydrocarbons and other organic molecules by $O^{\bullet-}$. A variety of interesting species have been formed in this way, such as *o*-benzyne anion from benzene,[2] bicyclobutene anion from bicyclobutane,[7] and tetramethyleneethane anion from 2,3-dimethyl-1,3-butadiene.[8] However, the mode of $H_2^{\bullet+}$ abstraction in these reactions is often unpredictable and uncontrollable, or it fails altogether.[9] Recognizing the great utility of the DePuy fluoride-induced desilylation procedure for regioselective synthesis of gas-phase carbanions from trimethylsilyl compounds,[10] we began exploring the reactions of $O^{\bullet-}$, $F_2^{\bullet-}$, and other radical anions with bis(trimethylsilyl) derivatives, $R(SiMe_3)_2$, as a potential means for producing the corresponding biradical negative ions, $R^{\bullet-}$. Although the reactions of bis(trimethlysilyl) compounds with these ions do not appear to yield any of the desired $R^{\bullet-}$ products, biradical negative ions are produced in high yields from reactions between trimethylsilyl-containing anions and neutral F_2 (Scheme 1). These reactions most likely occur by dissociative electron transfer to F_2 within the ion/molecule collision complex to yield a trimethylsilyl-substituted radical and F^-, followed by fluoride-induced desilylation of the radical to produce the corresponding biradical negative ion. Analogous reactions are also observed with NF_3, although with lesser yields.[11]

Scheme 1



For example, electron impact ionization or fluoride-induced desilylation of either *m*- or *p*-bis(trimethylsilyl)benzene produces the corresponding (trimethylsilyl)phenyl anions. Reaction of these ions with F_2 (5% in helium) added downstream in the flow tube yields intense ion signals due to $C_6H_4^{\bullet-}$ (*m/z* 76), along with lesser amounts of $C_6H_5^-$ (*m/z* 77) and $C_6H_3^-$ (*m/z* 75) ions formed as primary and/or secondary products. The $C_6H_4^{\bullet-}$ ions produced in this way are readily distinguished from the lower-energy *o*-benzyne anion by their characteristic reactivity. For example, both **1** and **2** react with CS_2 by sequential abstraction of two sulfur atoms (eq 1), whereas the *o*-isomer reacts only by electron transfer.[2] Similarly, **1** and **2** react with nitric oxide by sequential addition of two NO molecules to produce the corresponding dinitrosobenzene radical anions, while *o*-benzyne ion does not appear to react with NO at all. Reactions of **1** and **2** with D_2O proceed mainly by neutralization, forming DO^-, attesting to their strong basicity ($\Delta H_{acid}(D_2O)$ = 392 kcal/mol[12]). In contrast, *o*-benzyne anion shows four sequential H/D exchanges with D_2O without neutralization ($\Delta H_{acid}(C_6H_5)$ = 379 kcal/mol).[2] Whereas **1** and **2** react with NO_2 almost entirely by electron transfer (EA(NO_2) = 54.2 kcal/mol;[13] EA(C_6H_5) = 25.3 kcal/mol[14]), the carboxylated forms of these ions, produced by addition of CO_2, give abundant adducts with NO_2 (Scheme 2). The acid–base

$$C_6H_4^{\bullet-}\ (\mathbf{1}\ \text{or}\ \mathbf{2}) \xrightarrow[-CS]{CS_2} C_6H_4S^{\bullet-} \xrightarrow[-CS]{CS_2} C_6H_4S_2^{\bullet-} \qquad (1)$$

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(11) EA(F) = 78.4 kcal/mol; EA(F_2) = 71.0 kcal/mol; DH[F–F] = 37.8 kcal/mol; DH[NF_2–F] = 57.3 kcal/mol, ref 12.

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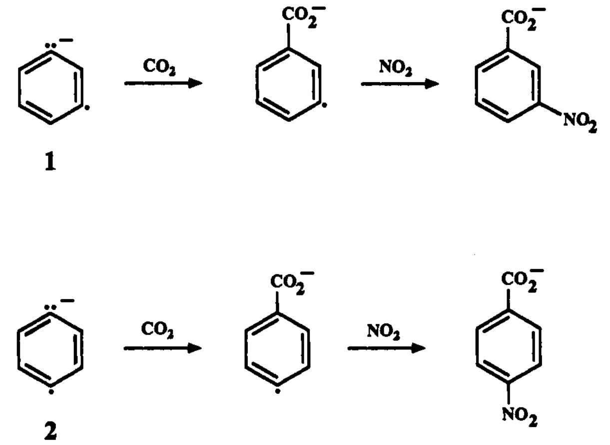
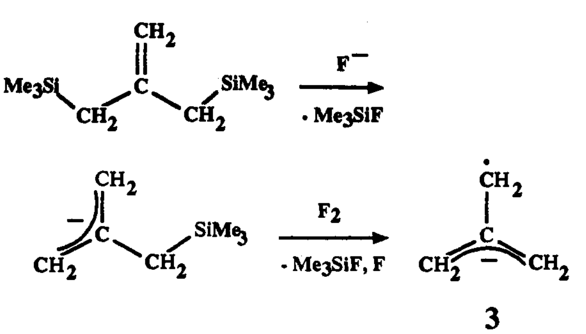
Scheme 2

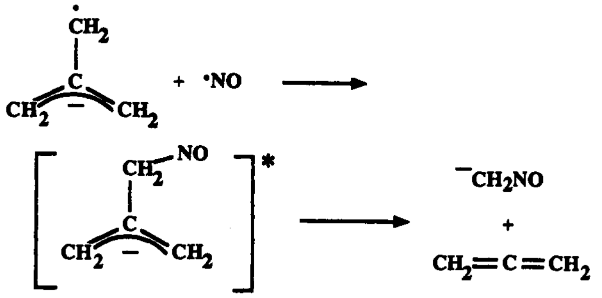


behavior[15] of the nitrobenzoates formed by this derivatization sequence is identical to that of authentic *m*- and *p*-nitrobenzoate ions produced by deprotonation of the corresponding nitrobenzoic acids, thereby confirming the structural assignments for **1** and **2**.



(2)

Trimethylenemethane anion (**3**) can be formed in high yield by the reaction sequence illustrated in eq 2. The observed reactivity of this ion is consistent with the behavior expected for a structure containing both allylic carbanion and radical moieties. For example, **3** reacts rapidly with N_2O to yield a $C_4H_4N_2^-$ product with *m/z* 80 arising by N_2O addition and H_2O loss, a characteristic reaction of allylic carbanions.[16] However, unlike allylic carbanions, which typically exchange all of their allylic hydrogens upon reaction with D_2O,[17] ion **3** appears to slowly incorporate only one or two deuterium atoms and reacts mainly by neutralization to produce OD^-. Ion **3** reacts with NO to yield CH_2NO^- (*m/z* 44) as the major ionic product. This is a novel reaction that may result from radical addition of the NO molecule to a CH_2 group followed by an E_{1cb}-like elimination of allene (eq 3). The reactions with N_2O and NO were repeated with **3**-d_2, which was generated from the reaction sequence shown in eq 2 with $CD_2{=}C(CH_2SiMe_3)_2$. Reaction of the labeled ion with N_2O produces $C_4H_4N_2^-$ (*m/z* 80) and $C_4H_2D_2N_2^-$ (*m/z* 82) from loss of D_2O and H_2O, respectively, in a 1:2 yield ratio. Similarly, **3**-d_2 reacts with NO to produce CD_2NO^- and CH_2NO^- in a 1:2 yield ratio. The occurrence of statistical yields of labeled and unlabeled products from these reactions indicates that the three methylene groups have become completely scrambled in ion **3**, either during its initial formation or as a result of a low-energy automerization of the Jahn–Teller distorted, C_{2v} structure expected for this species.[18]



(3)

The biradical negative ion synthesis procedure appears to be general in scope, limited only by the stability of the product and the availability of an appropriate trimethylsilyl-containing carbanion precursor with an electron binding energy sufficiently low to allow the initial dissociative electron-transfer step to take place (Scheme 1).[11] Thus, we have been able to produce a number of other novel species with this method, including the oxyallyl anion, $CH_2C(O)CH_2^{\bullet-}$, from 2-(trimethylsiloxy)allyl anion, the acetate radical anion, $CH_2C(O)O^{\bullet-}$, from trimethylsilyl acetate enolate, and the propadienylidene anion, $CH_2CC^{\bullet-}$, from 1-(trimethylsilyl)propargyl anion. Further details concerning the generation and characterization of these species are forthcoming.

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[15] Determined by collision-induced dissociation of the proton-bound dimers formed with difluoroacetic acid, i.e., by the Cooks kinetic method; c.f.: Wright, L. G.; McLuckey, S. A.; Cooks, R. G. *Int. J. Mass Spectrom. Ion Phys.* **1982**, *42*, 115. ΔH_{acid}(*m*-nitrobenzoic acid) = 330.2 ± 2.1 kcal/mol; ΔH_{acid}(*p*-nitrobenzoic acid) = 328.2 ± 2.2 kcal/mol; $\Delta H_{acid}(CHF_2CO_2H)$ = 331.0 ± 2.2 kcal/mol, ref 12.

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[18] QCISD(T)/6-31+G(d)//UMP2(fc)/6-31+G(d) calculations indicate a nearly degenerate $^2B_1$ and $^2A_2$ (C_{2v}) ground state for 3, with a barrier for pseudorotation via the D_{3h} structure less than 2 kcal/mol and a CH_2 rotational barrier less than 9 kcal/mol.